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Published in:
Physica B

DOI:
10.1016/S0921-4526(96)00793-4

ELSEVIER

Physica B 230–232 (1997) 1017–1020

PHYSICA B

Spins and phonons in the spin-Peierls compound $CuGeO_3$

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Abstract

Vibrational and spin dynamical properties of $CuGeO_3$ are studied using inelastic light scattering techniques as a function of temperature and magnetic field. Apart from one phonon processes, also two phonon scattering has been observed. Two spin gaps are observed in the dimerised phase, which disappear in the high field incommensurate phase. Raman data show that well-defined propagative modes still exist in the high field phase, whereas infrared absorption shows the presence of a new gap which is attributed to the Zeeman splitting of the ground state in the high field phase.

Keywords: Inelastic light scattering; Spin-Peierls system; $CuGeO_3$

1. Introduction

$CuGeO_3$ is the first magnetoelastic inorganic compound in which a spin-Peierls (SP) transition has been observed [1]. From a magnetic point of view $CuGeO_3$ can be described as a quasi-one-dimensional isotropic Heisenberg antiferromagnet, where the magnetic chains are formed by Cu^{2+} ions running along the *c*-axis of the orthorombic structure. The field/temperature phase diagram of $CuGeO_3$ [2] comprises a uniform (U) phase at high temperatures ($T > 14$ K), a dimerised (D) or spin-Peierls phase at low temperatures and low fields ($B < 12.5$ T), and an incommensurate (IC) or soliton phase [3–5] at low temperatures and high fields. In the U phase, one may to further distinguish [6] a true high temperature (HT, $T > 60$ K) regime without any short-range magnetic order, and a low-temperature regime in which short-range magnetic order (SRO) is present.

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2. Phonons

Fig. 1(a) shows polarised Raman spectra of $CuGeO_3$ recorded at $T = 295$ K using a CCD equipped spectrometer with the 514 nm line of an Argon laser as excitation source. All allowed one phonon scattering processes are observed in the spectra. The selection rules [7] are well obeyed, and no evidence is found for symmetry breaking due to resonant processes, as suggested in Ref. [7]. We did, however, find a strong wavelength dependence of the *overall* scattered intensity, which we believe to originate from the pronounced minimum around 2.4 eV in the absorption spectrum of $CuGeO_3$ [8].

The dimerisation of the lattice in the D phase leads to a superstructure with a fourfold unit cell, and to a more than doubling of the number of allowed Raman active phonons [9]. Neutron experiments [10], however, have shown that the actual atomic displacements are fairly small ($< 0.1\%$). One thus expects only weak scattering from the additional modes. Experiments [6, 9, 12] indeed show only three newly activated modes in the D phase at 106, 369, and 820 cm^{-1} (see also Fig. 1(b)). They are all found in the

PII S0921-4526(96)00793-4

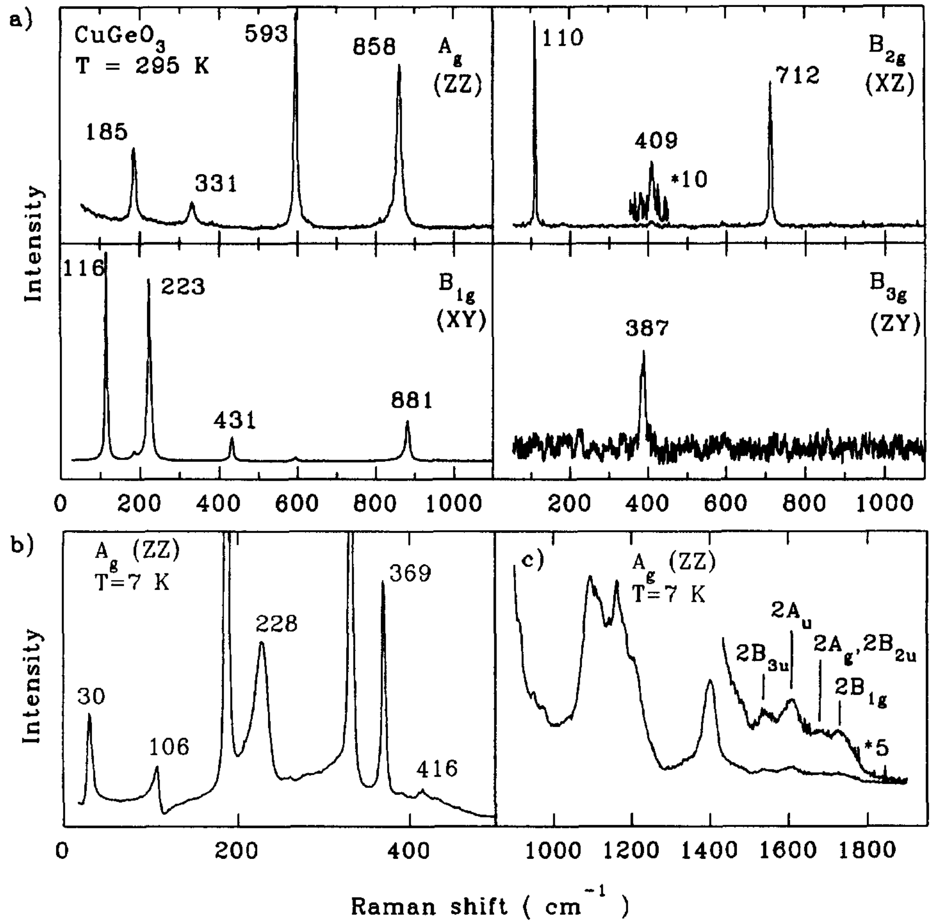

Fig. 1. (a) Polarised Raman spectra of $CuGeO_3$ at $T = 295$ K. The peak frequencies are indicated in cm^{-1}. (b) Raman spectrum recorded in (ZZ) geometry at $T = 7$ K (spectrum is blown up by a factor 8 with respect to Fig. 1(a). (c) Two phonon spectrum of $CuGeO_3$ in (ZZ) geometry recorded at $T = 7$ K.

(ZZ) geometry, the only one which also shows magnetic scattering [6, 9, 12]. The observation of these modes already a few degrees above the phase transition, as well as in Si-doped samples which show no dimerisation, indicates that the activations are not due to the lattice distortion. As an alternative we here propose that the activity is induced by the development of a pronounced short-range order in the spin system, which, due to the importance of spin-phonon interactions, essentially leads to a double periodicity for the phonons involved.

In an early report Sugai [11] reported on a high-energy scattering band, extending from 500 to $2000\,cm^{-1}$, which was assigned to two magnon scattering. We did not observe this high-energy band in our samples. Instead we found a different structure which appears only in a A_g geometry (see Fig. 1(c)). Its temperature dependence, a comparison of the observed peaks with the energies of two phonon processes, as well as a determination of the selection rules, leads to assign the observed scattering to two phonon process. Definite assignments for the peaks observed below $1500\,cm^{-1}$ are, however, difficult. Above $1500\,cm^{-1}$ the situation is more clear since here only a few two phonon processes are possible (see Fig. 1(c)). Note in particular the peak around $1610\,cm^{-1}$ which cannot be accounted for by fundamental peak frequencies observed in optical experiments, and may be assigned to an overtone of one of the A_u modes.

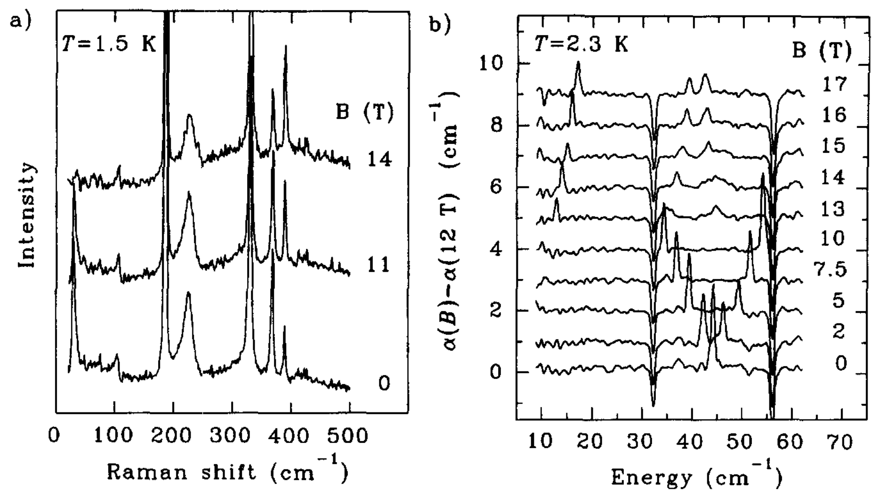

Fig. 2. (a) Raman spectra of $CuGeO_3$ recorded in a (ZZ) geometry at $T = 1.5\,K$ for $B = 0$, 11, and 14 T. (b) FIR absorbance difference spectra $\alpha(B) - \alpha(12\,T)$ at $T = 2.3\,K$. The negative peaks at 32 and $56\,cm^{-1}$ in all spectra are due the response of this triplet state in the 12 T spectrum.

3. Spin excitations

Several authors have reported on the observation of two-spin excitation Raman scattering in $CuGeO_3$ [6, 9, 12]. At high temperatures ($T > 60\,K$), in the HT regime, a strong central peak is observed, indicating a quasi-diffusive behaviour of the spin excitations. At lower temperature, in the SRO regime, the Raman intensity is transferred to higher energy with a maximum at $228\,cm^{-1}$ due to the formation of the spin wave continuum. The spin excitations in the D phase ($T < 14\,K$) are found to be well described by magnon like modes. The opening of the spin gap leads to a strong peak at $30\,cm^{-1}$, and the $228\,cm^{-1}$ maximum becomes much more pronounced.

Fig. 2(a) shows the (ZZ) Raman response of $CuGeO_3$ at $T = 1.5\,K$ in the dimerised ($B = 0$, 11 T) and high field ($B = 14\,T$) phases. For fields below the first-order phase transition to the IC phase no drastic changes are observed in the spectra. In particular, neither the gap at $30\,cm^{-1}$, nor the maximum at $228\,cm^{-1}$, show any splitting, consistent with expectations that only $S_z = 0$ two magnon states are Raman active [13]. For fields above the D–IC transition more drastic changes are observed. In the first place the pronounced gap response has disappeared, or has shifted to below $20\,cm^{-1}$. Secondly the intensity of the 106 and $369\,cm^{-1}$ phonons abruptly decreases at the phase transition. Thirdly, the $228\,cm^{-1}$ peak remains present (though weakened) above the phase transition, indicating the persistence of well-defined propagative modes in the IC phase.

In order to further investigate the spin dynamics in the IC phase we performed field-dependent ($B \parallel a$), unpolarised infrared transmission spectroscopy on a (1 0 0) oriented $CuGeO_3$ platelet ($d \approx 0.6\,mm$) at $T = 2.3\,K$. Fig. 2(b) shows the results obtained in various fields, plotted as the difference in absorbance α with a spectrum recorded at 12 T. In zero field, a single peak is observed at $44.3\,cm^{-1}$. As the field increases this peak splits linearly ($g = 2.13$), consistent with a triplet nature for the excitation responsible for this absorption. The observed splitting, together with the temperature dependence, shows that this mode is in fact the zone centre spin gap of $CuGeO_3$ [5]. Above the phase transition to the IC phase this triplet response has disappeared. Instead a new low-energy absorption peak is observed, which energy increases linearly with field ($g = 2.03$). One expects that the new ground state in the IC phase no longer has a singlet nature. The newly observed low-energy peak is therefore assigned to transitions between the two lowest-energy levels of the Zeeman split magnetic ground state. Finally, we note that there are several other new absorption peaks observed in the IC phase, which arise due to the incommensurability of both the lattice and the magnetic structure in this phase, as has been discussed in detail in Ref. [5].

4. Conclusions

The most important conclusions to be drawn from the present work are:

1. The vibrational selection rules are well obeyed.

2. The distorted $106\,cm^{-1}$ response in the Raman spectrum is confirmed to be due to a phonon, which couples to the spin excitations.

3. The activation of phonons in the D phase is likely due to the development of SRO in the spin system.

4. Well-defined propagative modes still exist in the IC phase, both near the zone centre, as well as near the zone boundary.

5. A new 'gap' is observed in the IC phase, arising from the Zeeman splitting of the ground state.

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